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(54) Method and apparatus for the production of mouldings from thermoplastic material whose partially crystalline state can be adjusted by physical effects, more particularly temperature effects

(57) Method for the production of mouldings from a thermoplastic material the crystallinity of which can be varied by varying one or more physical parameters, for example temperature, by:

forming a semifinished article, stabilizing the semifinished article by cooling of at least one surface thereof, thermally conditioning the stabilized semifinished article to render it thermally deformable, and thermal deforming the thermally conditioned article to obtain a stable moulding,

characterised in that the material is such that its crystallinity can be varied between amorphous and partially crystalline states and both the desired crystallinity and also a desired temperature gradient over a cross-section of the semifinished product are established in a wall portion of the semifinished article between the forming and stabilization steps by a first thermal conditioning operation, and in that a second thermal conditioning operation is carried out during the thermal deformation step with control of temperature to produce or maintain the desired final crystallinity in the plastics material of the said wall portion.

GB 2 059 328 A

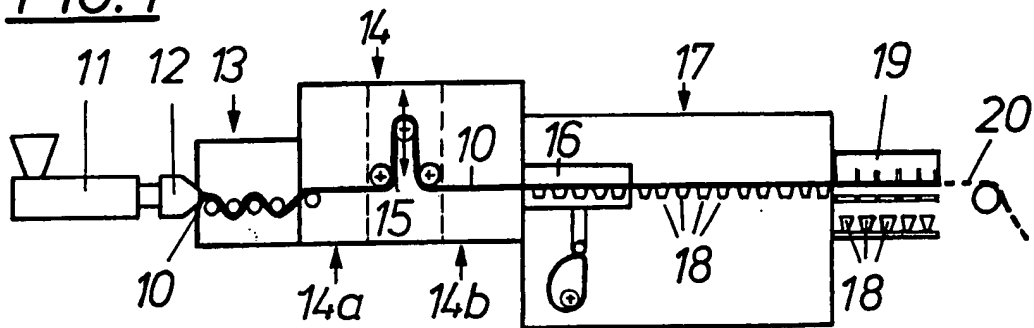
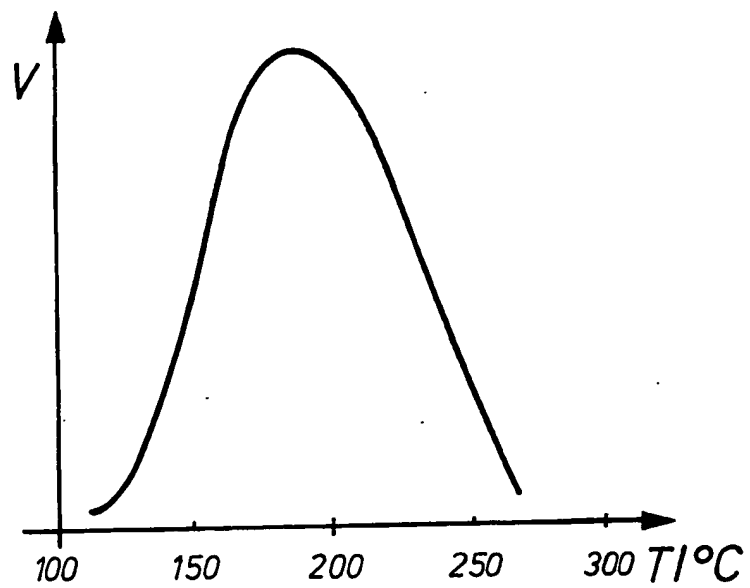
FIG. 1FIG. 2

FIG. 3

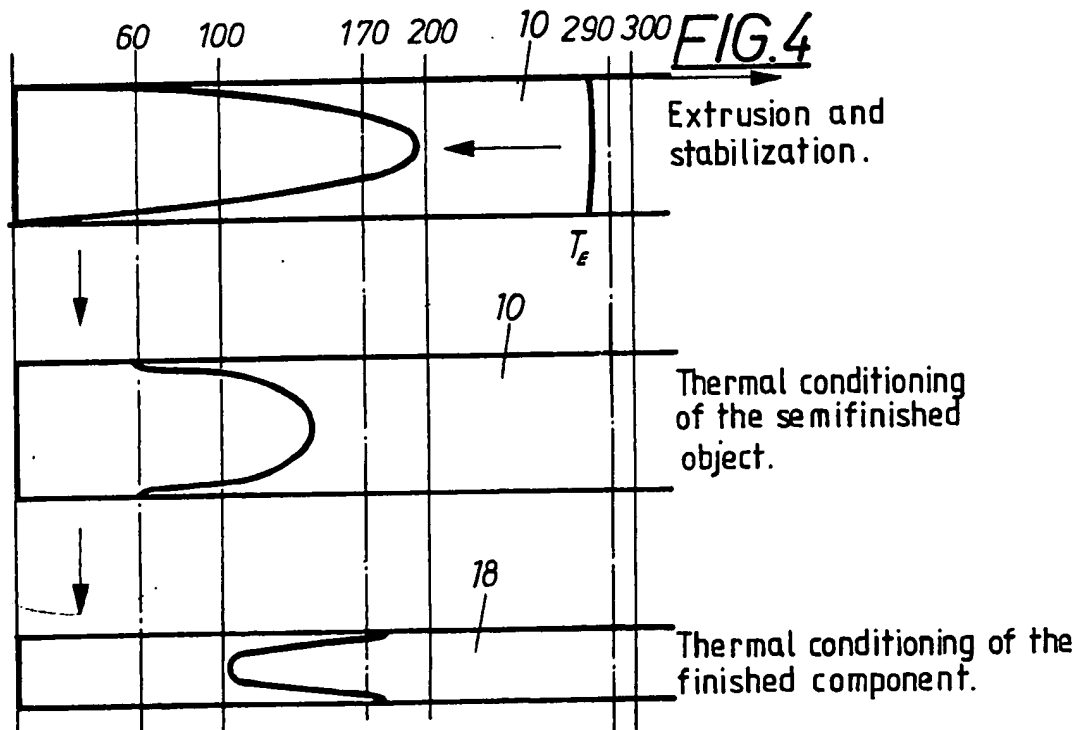
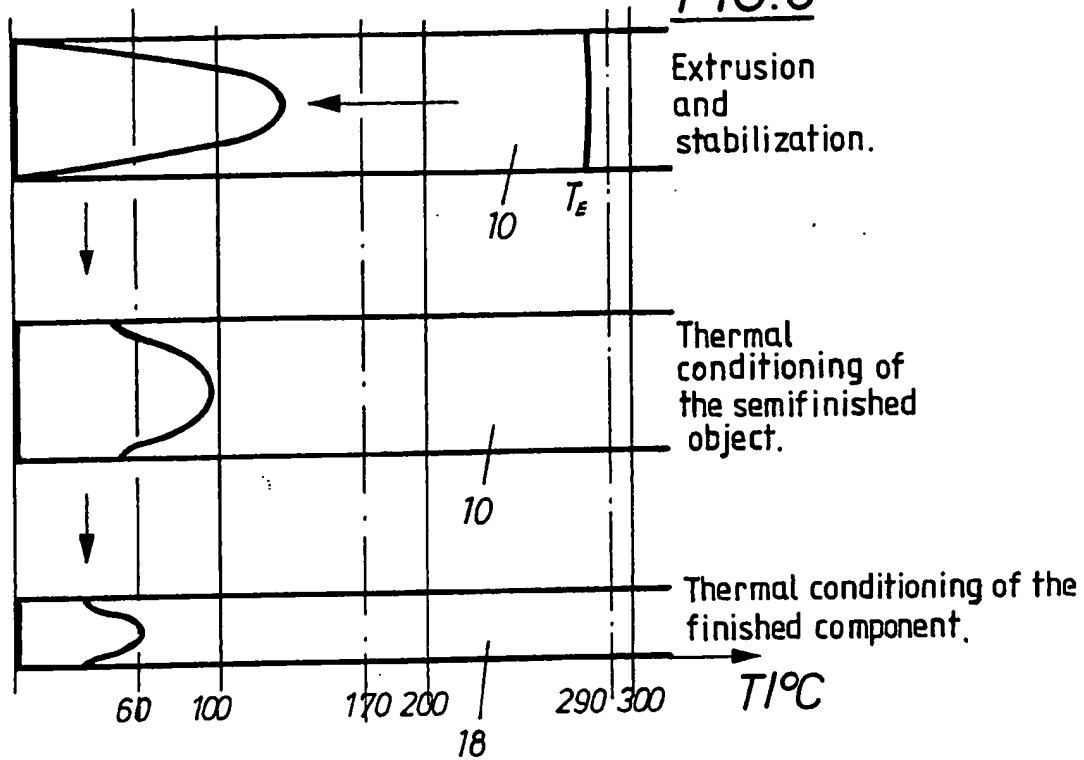


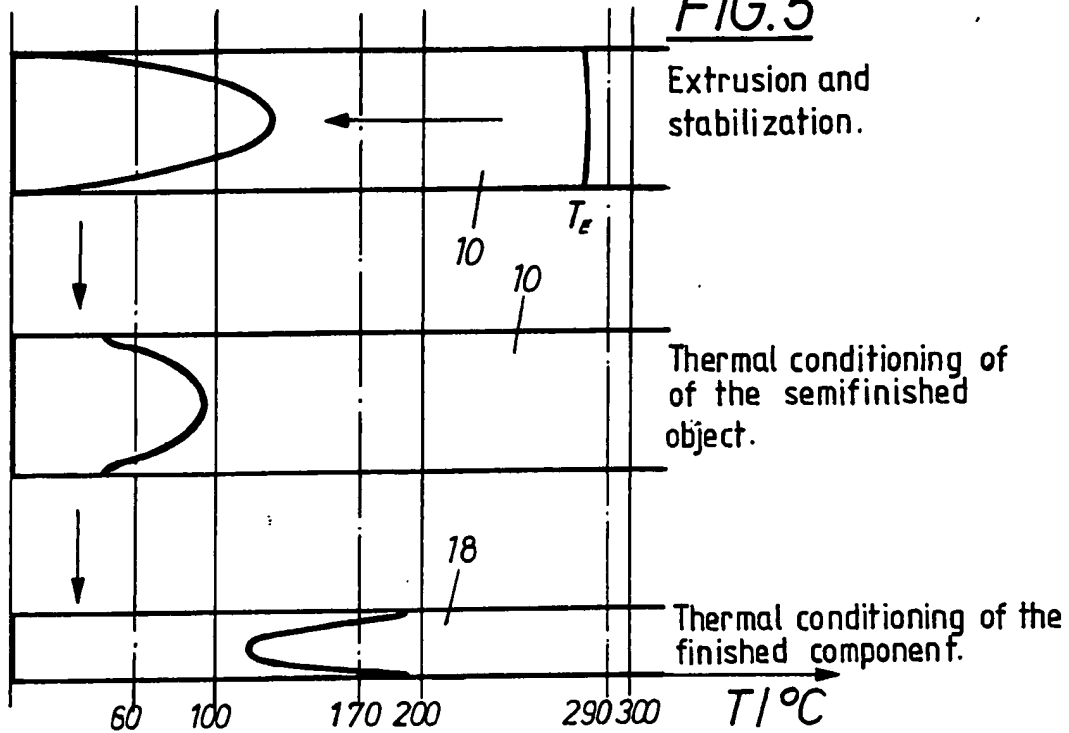
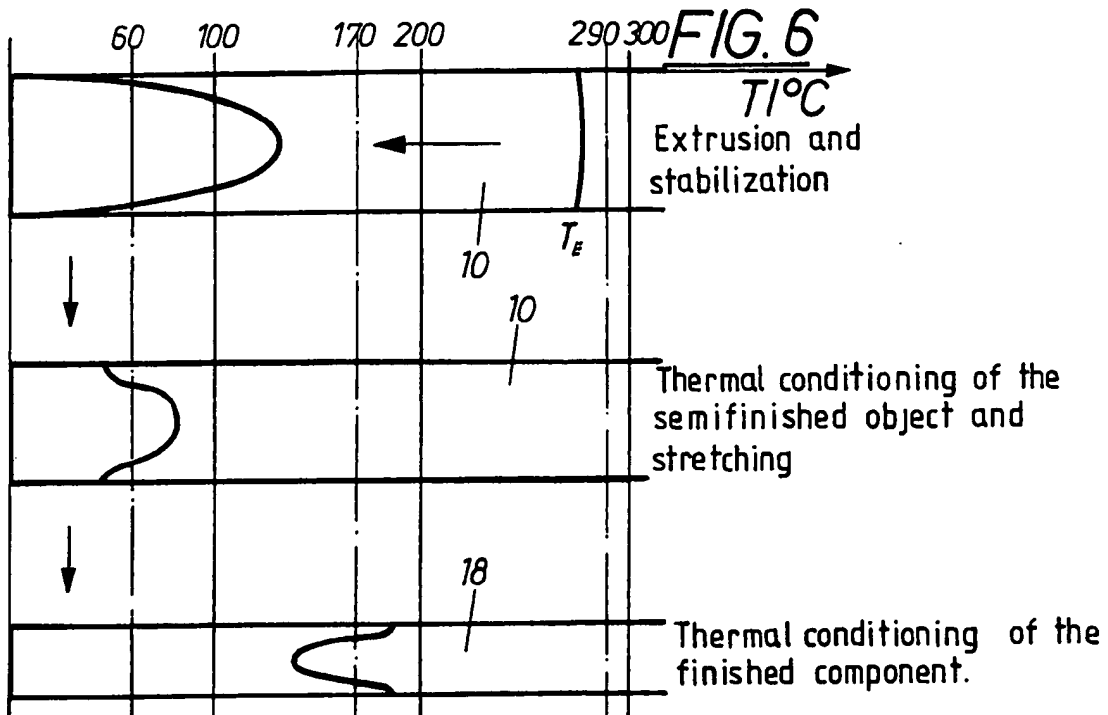
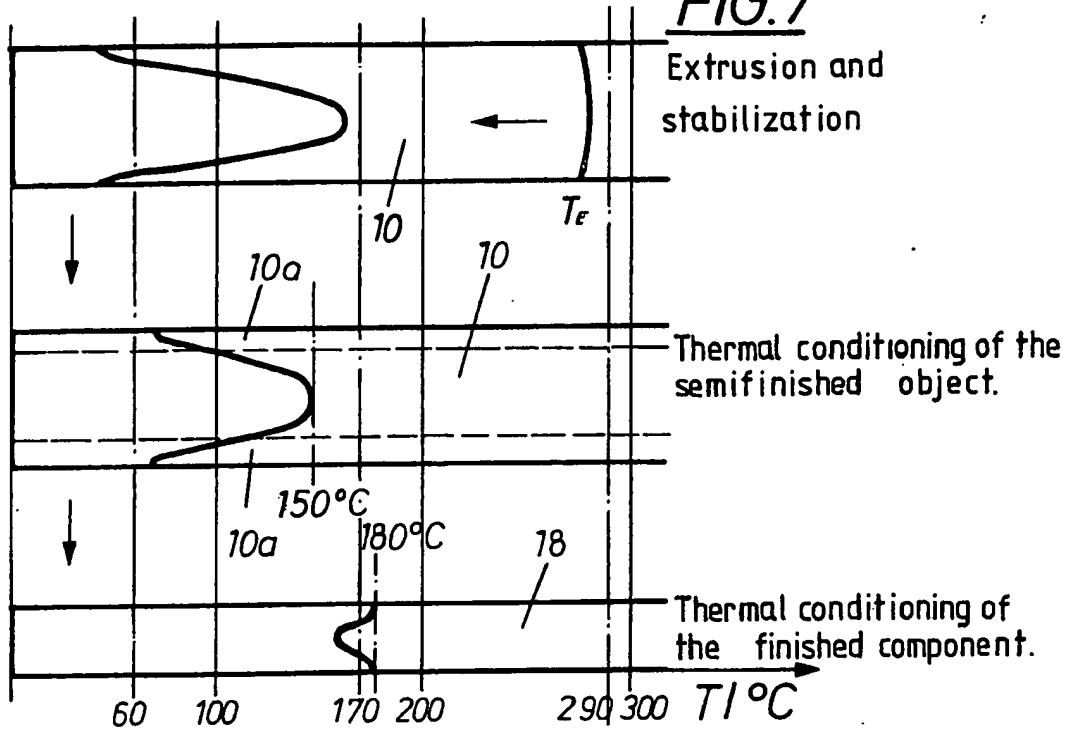
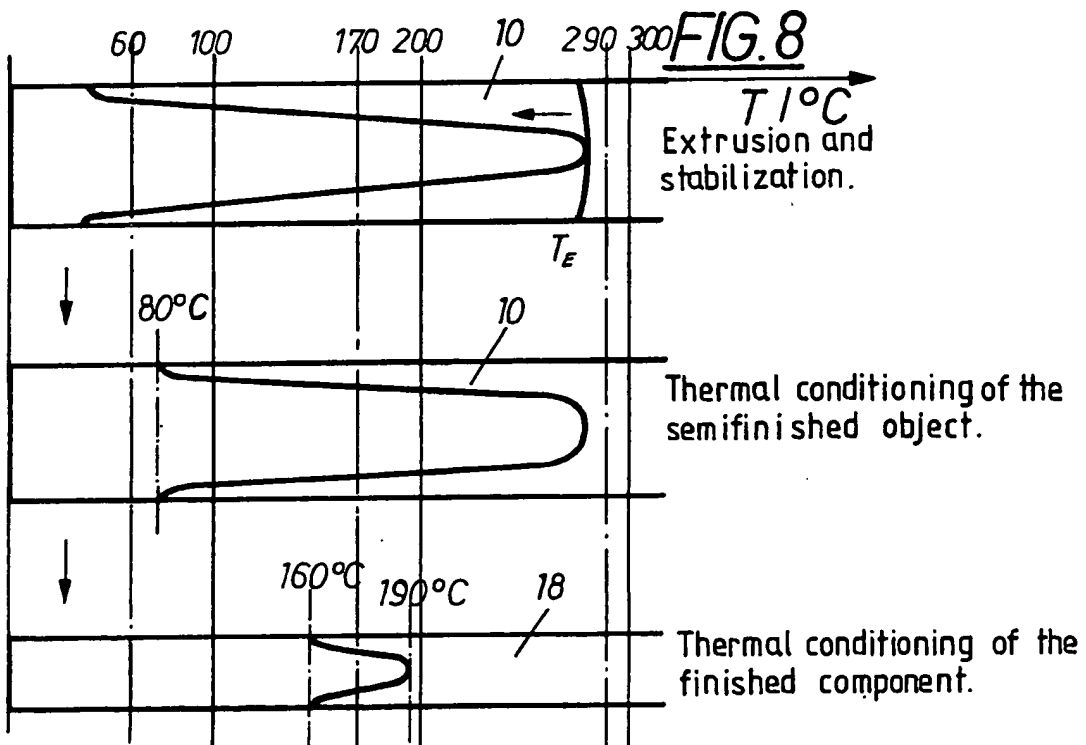
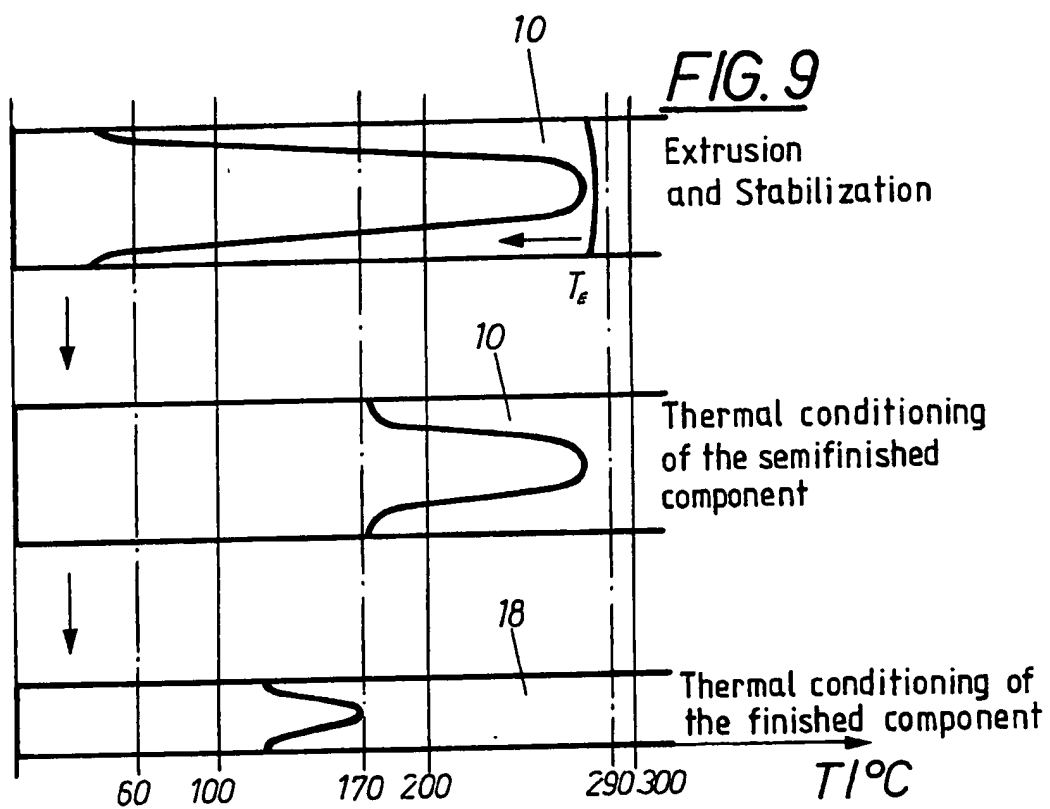
FIG. 5**FIG. 6**

FIG. 7**FIG. 8**



SPECIFICATION

Method and apparatus for the production of mouldings from thermoplastics material whose partially crystalline state can be adjusted by physical effects, more particularly temperature effects

The invention relates to a method and apparatus for producing mouldings from thermoplastics material whose partially crystalline state can be adjusted by physical effects, more particularly temperature effects, by:

Forming a semifinished material, more particularly continuous extrusion of a strip or tube of plasticized plastic,

Stabilization of the semifinished material by cooling of at least one surface,

Thermal conditioning of the stabilized semifinished material to produce thermal deformability and

Thermal deformation to produce form stable final mouldings from the semifinished material.

The German Offenlegungsschrift 28 30 740 and the German Offenlegungsschrift 28 30 788 disclose methods for the production of thin-walled articles of crystalline thermoplastics material. The thermoplastics material which is processed by these methods, more particularly polyolefin, is exclusively of a crystalline nature in every case and therefore merely offers the means for adjusting the partially crystalline state of the moulding wall to a greater or lesser crystalline degree and to influence the crystals contained in the plastics material of the moulding wall by temperature control and by utilizing physical effects. Accordingly, these known processes are designed to control the crystallinity of the plastics material and to physically influence the crystals in the plastics during production of the mouldings in such a way as to achieve an optimum approach to the desired properties of the moulding wall while at the same time providing useable conditions for thermal forming.

The British Patent Specification 1 514 277 also discloses the production of mouldings, more particularly bottles, of polyester material, by combined injection moulding and blow forming. According to this method a preform is first produced by injection moulding and its external surface is stabilized by cooling. First expansion by stretching of the cooled wall region and then complete moulding by blow forming is to take place thereafter. This known method is relatively complicated, occupies a substantial amount of time and cannot be performed continuously accompanied by the formation of a semifinished object.

By contrast, it is the object of the invention to provide a method and apparatus enabling the user to adjust the plastics material in the moulding wall to be either amorphous or to have a desired crystallinity state and crystallinity degree combined with desired physical properties, for example a desired elasticity, tensile strength and/or temperature form stability of the moulding when processing plastics materials which can be optionally adjusted to be amorphous or partially crystalline by means of

physical effects, more particularly temperature effects.

According to the invention, this problem is solved by using the following process features, namely in that

In the production of mouldings from such plastics material, whose crystallinity state can be optionally adjusted between amorphous and partially crystalline, the desired crystallinity condition is produced in the moulding wall by a first thermal conditioning operation to be performed on the semifinished material and by a second thermal conditioning process to be performed on the moulding; the physical effects to be performed in the course of the first thermal conditioning operation between stabilization and thermal forming are adapted and modified in predetermined manner to give a desired preparatory crystallinity and thermal deformability of the semiproduct plastics, and a temperature gradient which prepares for the desired final crystallinity state in the plastics material of the moulding wall and is adapted to the ensuing thermal deformation process, is adjusted over the cross-section of the semifinished object and

The second thermal conditioning process is carried out during the thermal deformation process and optionally ensuing thereon with temperature control to produce or maintain the desired final crystallinity state in the plastics material of the moulding wall in conjunction with obtaining form stability.

On the other hand, the method according to the invention offers a plurality of optionally modifiable and adjustable process parameters which influence the final crystallinity state of the plastics material in the moulding wall and the physical properties essential for the use of the moulding in a reproducible and precisely predefinable manner. The effective application and combination of the process parameters in use, more particularly of the heat treatment during the process, becomes particularly advantageous by the use of two thermal conditioning processes. Furthermore, the method according to the invention also offers the means of incorporating additional physical treatment steps such as stretching, rolling, calendering, consolidation, irradiation, electrostatic treatment, electromagnetic treatment and the like without in any way impairing the stability of the production process and the desired stable adjustment of the crystalline state in the plastics material of the moulding wall. The two thermal conditioning operations also offer advantageous application and combination facilities for these additional physical treatment steps.

A fundamental process possibility provided within the scope of the invention provides that

During stabilization and the first thermal conditioning process and while the desired final crystallinity state is adjusted, the semifinished object is cooled over its entire cross-section to a temperature at which no further substantial change of crystallinity state occurs in the plastics and temperatures at which no substantial changes of the crystallinity state occur are also maintained when the temperature gradient is adapted to the requirements of thermal forming in all regions of the semifinished

object and

Deep drawing and a second thermal conditioning process to fix the crystallinity state in the plastics material of the moulding wall thus formed and consolidated takes place in the course of thermal forming.

In this fundamental procedure made possible within the scope of the invention the final crystallinity state which is desired in the plastics material of the moulding wall is substantially adjusted at an early stage, namely during stabilization and during the first thermal conditioning process of the semi-finished object and is retained until the mouldings are substantially completed.

This fundamental process can be utilized to adjust a substantially amorphous state in the plastics material of the semifinished object during stabilization and the ensuing first thermal conditioning process and such substantially amorphous state can be retained substantially during the second thermal conditioning process, including the thermal forming process. Mouldings produced in this manner have plastics material in their wall in a practically amorphous state and are characterised by a relatively high degree of elasticity and flexibility. On the other hand they have only a relatively low temperature form stability.

Another fundamental method of performing the process within the scope of the invention is arranged so that

During stabilization and during the first thermal conditioning process the semifinished object is rapidly cooled over its entire cross-section and is adjusted to a temperature gradient which permits thermal forming but maintains temperatures in all regions of the semifinished object which are such that no substantial change of the crystallinity state occurs in the appropriate plastics material;

Thermal forming takes place on at least one mould surface which is heated to a temperature at which crystal growth occurs in the appropriate plastics material and

The temperature and duration of the second thermal conditioning process which takes place or commences when the moulding wall comes into contact with the heated mould surface, is adapted to obtain a desired partial crystallinity of the plastics material in the moulding wall.

In this method of performing the process a crystallinity state is adjusted in preparatory manner in the plastics material of the semifinished object and the desired final crystallinity state in the moulding wall is produced by thermal forming, proceeding from the said crystallinity state. During the first thermal conditioning process the plastics material of the semifinished object can be maintained substantially in the amorphous state. It is however, possible to subject the plastics material of the semifinished object to a first slight crystal growth during the first thermal conditioning process. The choice of one or the other possibility depends inter alia on the desired final crystallinity state in the plastics material of the moulding wall and on the degree of crystal growth desired during thermal forming.

To produce the desired degree of crystal growth

during thermal forming it is possible for the mould surface to be maintained at a temperature in the region from below to above the temperature for optimum crystal growth in the appropriate plastics material. To obtain the highest possible degree of crystal growth during thermal forming with a suitable short thermal deformation time, the mould surface must be held at a temperature in the region of the temperature for optimum crystal growth in the appropriate plastics material and where appropriate in the upper part of such a temperature range so that the temperature suitable for optimum crystal growth is adjusted as quickly as possible in the plastics material. If during stabilization and the first thermal conditioning process of the semifinished object in the process according to the invention the temperature conditions are such that practically no changes or only very slight changes of the crystallinity state occur, it is possible to subject the semifinished object to stretching, for example biaxial stretching, as an additional physical process during the first thermal conditioning process and/or between the first thermal conditioning process and thermal deformation while the crystallinity state of its plastics material is practically maintained. Such stretching can be applied when the plastics material is in a practically amorphous state or when the plastics material is in a partially crystalline state. Within the scope of the method according to the invention such stretching provides the surprising effect that high strength, high elasticity and a high degree of temperature form stability are combined in mouldings produced with this additional physical effect.

In another possibility for performing the method according to the invention

The surface regions of the semifinished object are adjusted during stabilization and the first thermal conditioning process to temperatures which are suitable for hardening to permit handling of the semifinished material and the interior is adjusted to temperatures allowing optimum crystal growth in the appropriate plastics material and

Thermal forming takes place on at least one mould surface which is heated to a temperature at which crystal growth occurs in the appropriate plastics material.

This modification of an embodiment of the method according to the invention is particularly suitable for cases in which the most substantial crystallization of the plastics in the moulding wall is desired. Mouldings produced in accordance with this modification of an embodiment of the method are characterised by a particularly high temperature form stability. With this performance modification of the method according to the invention it is however appropriate that the plastics material in the interior of the semifinished object is adjusted by the effect of the preset temperature and by the duration of the first thermal conditioning to form a crystallinity state in which the appropriate plastics material is still thermally deformable. If desired, the plastics in the interior of the semifinished object can also be converted into a crystallinity state which is beyond the limit of the actual thermal deformability of the appropriate plastics material, namely by the effect of

the present temperature and the duration of the first thermal conditioning process. The surface regions of the semifinished object in such a case are maintained in a more or less amorphous state or in an only slightly partially crystalline state and form sufficiently durable shells during the thermal forming process, between which shells the plastics material in the interior of the semifinished object, already crystallised outside the actual thermal deformability, can still be reliably deformed. In the last-mentioned means of embodying the method according to the invention it is particularly advantageous to heat the mould surfaces to a temperature allowing optimum crystal growth in the appropriate plastics. This results in a final heating through of the entire plastics material of the moulding wall thus formed and thus results in uniform crystallization.

Other means for performing the method according to the invention provide that

During stabilization and the first thermal conditioning process the cross-sectional surface regions of the semifinished object are adjusted to temperatures suitable for hardening to facilitate handling of the semifinished object while the interior is left substantially at the plasticizing temperature which was used for the extrusion of the material web;

Thermal forming is performed on at least one mould surface which is heated to a temperature at which crystal growth occurs in the appropriate plastics material and

For the second thermal conditioning process the moulding wall is maintained at a temperature at which crystal growth takes place in the plastics material of the moulding wall, namely for a period of time adapted to the desired final crystallinity state of the moulding wall.

With this method of performing the process, which is possible within the scope of the invention, the plastics material in the interior of the semifinished object is maintained at a temperature which is above the temperature region in which crystal growth occurs in the appropriate plastics. The surface regions of the semifinished objects on the other hand are substantially cooled so that the crystalline state thereof, for example an amorphous state or a slightly partial crystalline state, is frozen in such regions. By contrast to conventional, in-line thermal forming processes, the actual thermal forming procedure is now accompanied by complete heating through of the entire formed moulding wall and adjustment of the desired more or less intensive partially crystalline state accompanies such heating through during thermal forming and during the second thermal conditioning process. Since the plastics in the interior of the semifinished object in this system of performing the process transfers substantial quantities of heat into the first thermal conditioning process and as far as the thermal forming process and the second thermal conditioning process, it is advantageous for the temperature on the mould surfaces to be adjusted slightly below the temperature for optimum crystal growth so that by these means more rapid cooling of the plastics material in the interior of the formed moulding wall is obtained in the particular temperature region in

which optimum crystal growth occurs.

In all modifications of the method according to the invention, in which crystal growth is permitted during the actual thermal forming process, the moulding wall can be maintained in contact with the mould surface until the plastics has reached the desired degree of crystallinity. It is however also possible to merely initiate crystal growth on the mould surface and to remove the moulding from the mould surface when adequate mould stability has been reached and to perform the second thermal conditioning process in a heat treatment device which adjoins the exit of the thermal forming device. The said second thermal conditioning process - commencing on the mould surface - can be performed at a uniform temperature. It is also possible to vary the temperature during the second thermal conditioning process, for example by heat treatment at a temperature which diminishes with respect to time. In the last mentioned kind of temperature control it is possible to commence with a mould surface temperature which is suitable for optimum crystal growth in the appropriate plastics material and the moulding wall can be cooled with respect to time.

In the method according to the invention the thermal forming process can be performed by applying mould pressure to the plastics material of the moulding wall. Where appropriate, such mould pressure can be selected so as to be suitable for a specific consolidation of the plastics material.

The method according to the invention also allows semifinished objects to be subjected to a calendering and/or rolling operation, accompanied by thickness reduction, between the extrusion and the thermal forming process as a means of applying an additional physical influence on the crystallinity state. Such calendering or rolling can be incorporated in the stabilization of the semifinished object.

The method according to the invention can be used advantageously for the production of mouldings from polyethylene terephthalate. It can also be considered for the production of mouldings from modified polyethylene terephthalate, for example 1,4-cyclohexyl dimethylene terephthalate/isophthalate - copolymer. The production of mouldings from polybutylene terephthalate by the method according to the invention is also feasible. In the last-mentioned case however it should be noted that the temperature region within which crystal growth occurs in polybutylene terephthalate extends downwardly, i.e. to approximately 30°C.

The method according to the invention can be performed by apparatus with an extruding device for the continuous production of the semifinished object, a stabilizing device for the semifinished object and a thermal forming device and a thermal conditioning device for the semifinished object and, where appropriate, a device for cutting out the mouldings for the surrounding parts of the semifinished object. According to the invention, such a device should be characterised by the following features:

A first thermal conditioning station is disposed between the stabilizing device and the thermal

forming device;

The thermal forming device is disposed in a second thermal conditioning station;

The stabilizing device and the thermal forming device are provided with control means for the predefined and where appropriate programmable regulation of the physical and more particularly thermal effects which act on the plastics material of the semifinished object and take place in the stabilizing device and in the thermal forming device and

The thermal conditioning stations are associated with means for producing physical, more particularly thermal effects on the plastics material of the semifinished object or moulding and said conditioning stations are also associated with control means for the predefined and where appropriate programmable regulations of the effect producing means.

A device of this kind offers the advantage that it permits practically all desired modifications of the method according to the invention to be performed without any substantial refitting steps. It also offers the advantage of enabling devices for special desired physical effects such as stretching, rolling, irradiation and the like to be incorporated without difficulty at any desired place in the apparatus.

The thermal conditioning stations of the apparatus according to the invention, more particularly the first thermal conditioning station for the semifinished object can be provided with heating and cooling means for the semifinished object or for the mouldings with regulating facilities for temperature and heating or cooling time. When equipped in this manner, thermal conditioning in the device according to the invention can be performed in all possible modifications of the method with complete reliability and optimum effectiveness.

The first thermal conditioning station, namely the station for the semifinished object, can also be associated with a stretching device for the semifinished object and regulating means for stretching temperature, degree of stretching and, where appropriate, stretching rate. Associating the stretching device with the first thermal conditioning station offers a special advantage in that the stretching operation is performed when the semifinished object is in a state in which optimum conditions for stretching itself as well as optimum conditions for the effect of stretching on the crystallinity state of the plastics material can be adjusted and can also be retained up to the thermal forming operation.

If additional devices for calendaring and/or rolling of a web-shaped semifinished object, accompanied by thickness reduction, are to be provided in the device according to the invention, these can be associated with the stabilising device.

The cooling means provided in the stabilizing device of the apparatus according to the invention can be provided with means for applying variable temperature control which acts on the plastics of the semifinished object in a timed sequence. This means that in a tandem arrangement of a plurality of cooling devices, these can be operated at different temperatures.

The thermal forming device in the apparatus

according to the invention should be provided with at least one mould having a variably heatable and coolable mould surface. Conveniently, the thermal forming device can contain at least one mould, at least one surface of which is equipped with control means for providing temperature change or temperature control which can be predefined or where appropriate can be programmed with respect to time during the thermal forming process. The thermal forming device can also contain at least one mould which is equipped with means for producing a predefinable, controllable mould pressure. The means for producing mould pressure can be equipped with control devices for controlling or where appropriate varying the mould pressure programmably with respect to time during the thermal forming process.

In the apparatus according to the invention the inlet region of the second thermal conditioning station can advantageously contain the thermal forming device and can extend beyond the exit of the thermal forming device. The second thermal conditioning station can have a moulding heat treatment device which adjoins the exit of the thermal forming device.

Exemplified embodiments of the invention are explained hereinbelow by reference to the accompanying drawings in which:

Figure 1 is a diagram showing the fundamental progress of the procedure according to the invention or the basic construction of apparatus according to the invention;

Figure 2 is a graph showing the crystal growth rate V plotted against the temperature T in the case of polyethylene terephthalate;

Figure 3 shows a group of temperature gradients for a first means of embodying the method according to the invention in conjunction with polyethylene terephthalate;

Figure 4 shows a group of temperature gradients for a second means of embodying the method according to the invention in conjunction with polyethylene terephthalate;

Figure 5 shows a group of temperature gradients for a third means of embodying the method according to the invention in conjunction with polyethylene terephthalate;

Figure 6 shows a group of temperature gradients for fourth means of embodying the method according to the invention in conjunction with polyethylene terephthalate;

Figure 7 shows a group of temperature gradients for fifth means of embodying the method according to the invention in conjunction with polyethylene terephthalate;

Figure 8 shows a group of temperature gradients for sixth means of embodying the method according to the invention with polyethylene terephthalate, and

Figure 9 shows a group of temperature gradients for seventh means of embodying the method according to the invention with polyethylene terephthalate.

Figure 1 illustrates the sequence of operations in a preferred embodiment of the method for producing

thin-walled articles from thermoplastics material which can be adjusted to be optionally amorphous or partially crystalline to a greater or lesser extent. In the illustrated example an extrusion press 11 is provided and is adapted to receive thermoplastics material, for example polyethylene terephthalate, to compress it continuously and to heat it until it is molten and is supplied at a temperature T_E (Figures 3 to 8) above the crystal melting point to the extrusion die, for example a wide slit die 12. In the present case, the wide slit die 12 produces a web-shaped semifinished object 10 which exits from the wide slit die 12 and is introduced into the stabilizing device 13. By cooling of at least one of its surfaces the semifinished object 10 is first rendered suitable in the stabilizing device 13 for handling to allow for the processing. From the stabilizing device 13 the web-shaped semifinished object 10 enters a first conditioning station 14. The principal purpose of the conditioning stage 14 for the semifinished object is to adjust preparatory temperature gradients therein. It is however also a purpose of the conditioning station 14 for the semifinished object 10 to apply additional desired physical effects or to fix additional physical effects which were previously applied to the semifinished object 10.

To this end, the conditioning station 14 for the semifinished object is provided with heating devices and cooling devices having regulating means which can be optionally controllable and where appropriate programmable. Furthermore, the conditioning station 14 for the semifinished object can be associated with means for physically influencing the semifinished object 10. Such means include stretching devices, irradiating devices, rolling and compacting devices. The last-mentioned devices can however also be already included in the stabilizing device 13.

In the illustrated example, the conditioning station 14 for the semifinished object is constructed in two stages, namely a first stage 14a for treatment, i.e. for thermal conditioning of the semifinished object 10 which passes through continuously, and a second stage 14b which is constructed for treatment and thermal conditioning of the semifinished object 10 which passes through intermittently. Between the two stages 14a and 14b of the conditioning station 14 for the semifinished object - incorporated into said conditioning station 14 - there is a device for controlling and converting the motion of the semifinished object 10 from a continuous feed to an intermittent feed. The feed motion of the semifinished object 10 is adapted by means of the device 15 to the operating cycle of the conditioning station 17 for the finished component and thermal forming device 16 adapted to receive the semifinished object 10.

The conditioning station 17 for the finished component or the second thermal conditioning station 17 contains the thermal forming device 16 in its first part, in the illustrated example equipped with deep drawing dies whose mould surfaces can be optionally heated or cooled and can also be adapted to change the temperature during each operating routine. According to the illustration of Figure 1, the

thermal forming device 16 is followed by a portion of the finished component-conditioning station 17 through which portion web-shaped semifinished material with formed mouldings 16 from the thermal forming device 16 pass intermittently in the illustrated example. Heating and cooling devices are provided in the said second portion of the finished component-conditioning station 17. Means for the physical treatment of the mouldings 18, for example for irradiation or for applying sound waves and the like can also be arranged in the said second portion.

The web-shaped semifinished objects with mouldings 18 formed therein pass from the second thermal conditioning station 17 to a punching device 19 by means of which the mouldings 18 are punched out and the residue 20 of the semi-finished object is discharged for material recovery or, where appropriate, for the direct return of the reduced material to the extrusion press 11.

The semifinished object 10, referred to above in exemplified form as plastics web, can have a thickness of approximately 2 mm when polyethylene terephthalate is being processed.

All other possible and continuously producible semifinished objects, for example, tubes, sectional strands and the like can also be considered in place of the web-shaped semifinished object. The semifinished object can also be laminated material comprising several plastics materials of which however a substantial proportion should be plastics which can be optionally adjusted to be amorphous or partially crystalline to a desired degree by the application of physical effects, more particularly by temperature control.

Pressure treatment of the plastics material can be performed on the semifinished object, for example by rolling or calendaring in the stabilizing station 13 or in the first part 14a of the conditioning station 14 for the semifinished object. It is however also feasible to perform pressure treatment on the plastics material by successive surface pressing during the intermittent progress through the second part 14b of the conditioning station 14 for the semifinished object. The invention also makes it possible to apply pressure treatment to the moulding or to the finished component, i.e. within the second thermal conditioning station 17. Such pressure treatment is applied advantageously to the finished component by applying a predefined mould pressure in the thermal forming device 16.

Ultrasonics treatment can be applied in place of pressure treatment or additionally thereto, either on the semifinished object or on the finished component. Pressure treatment or ultrasonic treatment not only influences the crystallinity state but also leads to substantially improved stiffness and therefore improved cold form stability of the mouldings thus produced.

The graph shown in Figure 2 shows the crystal growth rate V of polyethylene terephthalate plotted against the temperature T in $^{\circ}\text{C}$. As indicated in Figure 2, between 100°C and the crystalline melting point (250 to 260°C) polyethylene terephthalate has a crystal growth-temperature range within which the optimum crystal growth occurs at approximately

170°C to 175°C. Above the crystalline melting point, polyethylene terephthalate changes into its plasticized state. At a temperature below 60°C polyethylene terephthalate occurs in the solid state without any substantial crystal growth occurring in the material. This means that cooling polyethylene terephthalate to a temperature below 60°C enables the prevailing crystallinity state of the material to be frozen.

- 10 In order to simplify the explanations the amorphous state can also be regarded as a crystallinity state within the scope of this application, namely a state of "crystallinity zero".

The method according to the invention is to provide economically advantageous means of producing mouldings of plastics with the above-described properties and the method is to provide means for selecting the final crystallinity state of the plastics material in the moulding wall. Fundamentally, this is achieved with the invention by producing a semifinished object through continuous extrusion at a temperature T_E (see also Figures 3 to 8) which is above the crystallinity melting point in a temperature range in which the material occurs in plasticized form, by utilizing the characteristics of the plastics under consideration as explained above in conjunction with Figure 2. Depending on the demands and requirements made on the moulding, the material is cooled and thermally conditioned from this plastics state in accordance with the crystal growth temperature range shown in Figure 2 so that on reaching the temperature range in which it occurs as a solid substance (below 60°C in the case of polyethylene terephthalate) the material has a desired crystallinity state combined with desired physical properties.

Some examples of possibilities which can be obtained by thermal conditioning in accordance with the invention are disclosed in the description hereinbelow referring to Figures 3 to 8.

- 40 In the example of Figure 3 relating to the production of mouldings from polyethylene terephthalate, the semifinished object 10 is intensively cooled during stabilization and during thermal conditioning is adjusted to a temperature gradient over the thickness of the semifinished object covering the region from 55 to 100°C in which there is practically no crystal growth or no crystal formation. The external regions or surface regions of the semifinished object can be cooled to below the aforementioned temperature region while the plastics material in the interior of the semifinished object can have a temperature of up to approximately 100°C, but should not exceed such temperature, at least not substantially. As indicated in the top part of Figure 3, the amorphous state in the plastics material can be substantially maintained or frozen during stabilization by rapid cooling to the temperature shown in the left-hand upper part of Figure 3, proceeding from the temperature gradient which prevails during extrusion and is at the extrusion temperature T_E . During the ensuing thermal conditioning (middle part of Figure 3) and the second thermal conditioning process (Figure 3, bottom part) which incorporates thermal forming, such temperature conditions can be maintained at and in the interior of the

- semifinished object 10 and the moulding 18 so that even then no substantial crystal growth or substantial crystal formation occurs. The molding thus produced is transparent, if it consists of pigment-free plastics, which means that the plastics material of the moulding wall is practically in its amorphous state. The temperature form stability of the moulding is approximately 70°C. If a certain degree of partial crystallinity is to be permitted or formed in the plastics of the moulding wall when adopting this method of operation, this can be achieved during stabilization and during the first thermal conditioning by cooling the semifinished object 10 more slowly and allowing partial crystallinity to occur to a desired degree. This partial crystallinity can be substantially retained in the plastics material of the moulding or finished component by suitable temperature control during thermal forming and during the second thermal conditioning process (see bottom part of Figure 3).

- Figure 4 illustrates means for controlling the method according to the invention by rapidly cooling the semifinished object 10 in order to consolidate its external regions or surface regions and to render these suitable for handling. The plastics material in the interior of the semifinished object however remains at a temperature which is distinctly above 100°C. The transition from the temperature gradient which occurs at the extrusion temperature T_E to the temperature gradient which is adjusted by stabilization can be seen by reference to the top part of Figure 4. During thermal conditioning of the semifinished object following on stabilization, it is possible to adjust a temperature gradient at which the external regions of the semifinished object are at temperatures at or slightly above 50°C and the core of the semifinished object is at temperatures above 100°C. With this kind of temperature control during stabilization and during the first thermal conditioning process there will be a substantial crystal formation and substantial crystal growth in the polyethylene terephthalate in the interior of the semifinished object 10, made manifest by clouding of the material. Since the length of time between conditioning of the semifinished object (middle of Figure 4) and thermal forming accompanied by conditioning of the finished component (bottom part of Figure 4) is fixed by the method according to the invention, the temperature gradient illustrated in the middle part of Figure 4, and the amount by which the temperature in the interior of the semifinished object 10 is above 100°C, permits predefinition of the degree of crystallization of the semifinished object at the commencement of conditioning of the finished component.

- Thermal forming in this example is performed by drawing the material on to a hot mould surface whose temperature should be between 120 and 180°C. A temperature on the mould surface of 180°C is assumed in the illustrated example. During conditioning of the finished component which commences during thermal forming and where appropriate continues beyond thermal forming, there will therefore be a substantial crystallization of the polyethylene terephthalate. The moulding will have

an opaque wall (when starting from pigment-free material). The temperature form stability of the moulding is above 200°C.

A similar process could be obtained in accordance with Figure 5 if stabilization and/or conditioning of the semifinished object under pressure results in a temperature gradient as shown in the upper and middle parts of Figures 3 and 5. If substantial crystallization of the plastics material is to be produced in such a case during conditioning of the finished component it would be necessary, proceeding from the nearly amorphous state of the polyethylene terephthalate, either to make available a longer time for crystallization or the degree of crystallinity achieved would be not as high as that obtained under the initial conditions according to Figure 4. As indicated by the bottom temperature gradient in Figure 5 it is possible in such a case to operate with a slightly higher temperature on the mould surface, for example up to 200°C. However, conditioning of the finished components after thermal forming can be extended in time as indicated in Figure 1 by the second thermal conditioning station 17. Mouldings produced in this manner have a transparent wall (when starting with pigment free material). The temperature form stability of the mouldings produced in this manner is approximately 150°C to 200°C.

Figure 6 shows means for controlling the method according to the invention but differing from Figures 3 or 5 by virtue of stretching of the semifinished object 10 being performed during conditioning of the semifinished object (see also middle part of Figure 6), i.e. between stabilization and thermal forming. As indicated by the middle temperature gradient in Figure 6, this stretching is accompanied by additional cooling of the semifinished object 10. During thermal forming, the semifinished object 10, which is stretched, more particularly biaxially stretched, is deep drawn on to the hot mould surface which can have a temperature of, for example, 150° to 200°C. In the example of Figure 6 a temperature of approximately 200°C is assumed on the mould surface of the thermal moulding die. Mouldings produced by the method controlled in accordance with Figure 6 also have a transparent wall (when starting with pigment free material) but a substantially improved temperature form stability, namely up to temperatures of 200°C to 250°C. Furthermore, mouldings produced in this manner are characterised by increased strength and elasticity.

In the example according to Figure 7 a temperature gradient in which relatively thick surface regions 10a are cooled to a temperature below 100°C and kept in the practically amorphous state of the polyethylene terephthalate, is adjusted on the semifinished object 10 during stabilization and subsequently during thermal conditioning. A maximum temperature of approximately 150°C is adjusted in the interior of the semifinished object 10. Proceeding from the temperature gradient illustrated in the middle part of Figure 7, thermal forming and conditioning of the finished component is performed on mould surfaces which are heated to approximately 150 to 180°C. In the illustrated example, the tempera-

ture of both mould surfaces, between which the moulding wall 18 is formed, amounts to 180°C. The plastics material of the moulding wall 18 is substantially crystallized between the two mould surfaces which are maintained at a temperature of 180°C. The moulding produced in this manner has a temperature form stability of approximately 200°C.

In the example of Figure 8 both surfaces of the semifinished object 10 are rapidly quenched during stabilization. A temperature between approximately 50 and 100°C is then adjusted on the surfaces of the semifinished object 10 during conditioning thereof while the polyethylene terephthalate in the core or in the interior of the semifinished object substantially retains the extrusion temperature, i.e. a temperature of approximately 270°C. The semifinished object having this temperature gradient (shown in the middle part of Figure 8) is thermally formed between two hot mould surfaces. To this end, the mould surfaces can have a temperature of 150 to 160°C. As can be seen by reference to the bottom part of Figure 8, a substantial equalization of the temperature gradient occurs between the mould surfaces. As a result, the polyethylene terephthalate in the surface regions of the formed moulding wall 18 is substantially crystallized at 160°C and the interior region of the moulding wall 18 is substantially crystallized at approximately 190°C, i.e. in the external regions slightly below and in the internal region slightly above the optimum crystallization temperature of approximately 170°C. Mouldings produced in this manner have opaque walls (when starting with pigment free material). The temperature form stability is approximately 200°C.

Figure 9 shows a modified method of operation in which the semifinished object is rendered suitable for handling during stabilization by rapid quenching of both surfaces. Conditioning of the semifinished object results in the adjustment of a temperature gradient which, as shown in the middle part of the illustration, is between the extrusion temperature (260° to 290°C) and approximately 170°C. A temperature gradient between 120°C and 170°C is adjusted on the moulding wall during thermal forming and conditioning of the finished component. Mouldings produced in this modified manner also have opaque moulding walls (when starting with pigment free material) and a temperature form stability of approximately 200 to 220°C.

Further to the above descriptions and in addition to the above-mentioned stretching, it is possible for other mechanical and physical treatments to be performed during conditioning of the semifinished object and accordingly during conditioning of the finished component, for example consolidation and thickness reduction by rolling or mould pressure, irradiation by means of rays of different kind, ultrasonics treatment and the like. The above-described means of embodying the method according to the invention can also be applied to semifinished objects of the most diverse kind, for example tubing, sectional strip and the like.

CLAIMS

1. Method for the production of mouldings from a thermoplastic material the crystallinity of which
5 can be varied by varying one or more physical parameters, for example temperature, by:
forming a semifinished article,
stabilizing the semifinished article by cooling of at least one surface thereof,
10 thermally conditioning the stabilized semifinished article to render it thermally deformable, and
thermal deforming the thermally conditioned article to obtain a stable moulding,
characterised in that the material is such that its
15 crystallinity can be varied between amorphous and partially crystalline states and both the desired crystallinity and also a desired temperature gradient over a cross-section of the semifinished product are established in a wall portion of the semifinished
20 article between the forming and stabilization steps by a first thermal conditioning operation, and in that a second thermal conditioning operation is carried out during the thermal deformation step with control of temperature to produce or maintain the desired
25 final crystallinity in the plastics material of the said wall portion.
2. A method according to claim 1 wherein the second thermal conditioning operation is continued beyond the thermal deformation step.
- 30 3. Method according to claim 1, characterised in that during stabilization and the first thermal conditioning process and while the desired final crystallinity state is adjusted, the semifinished object is cooled over its entire cross-section to a temperature
35 at which no further substantial change of crystallinity state occurs in the plastics and temperatures at which no substantial changes of the crystallinity state occur are also maintained when the temperature gradient is adapted to the requirements of
40 thermal forming in all regions of the semifinished object and
Deep drawing and a second thermal conditioning process to fix the crystallinity state in the plastics material of the moulding wall thus formed and
45 consolidated takes place in the course of thermal forming.
4. Method according to claim 3, characterised in that during stabilization and the first thermal conditioning process and while substantially maintaining
50 the amorphous state in the plastics the semifinished material is rapidly cooled to a temperature at which no substantial change of the crystallinity state occurs.
5. Method according to claim 3 or 4, characterised in that the mouldings are produced from polyethylene terephthalate and the temperature in the material web during stabilization and the first thermal conditioning process is adjusted to a range of 50 to 100°C.
- 60 6. Method according to claim 1, characterised in that during stabilization and the first thermal conditioning process the semifinished object is rapidly cooled over its entire cross-section and adjusted to a temperature gradient which permits thermal forming but maintains in all regions of the semifinished

object such temperatures at which no substantial change of crystallinity state occurs in the affected plastics;

- 70 Thermal forming is applied to at least one mould surface which is heated to a temperature at which crystal growth occurs in the appropriate plastics and
The second thermal conditioning process which takes place or commences by contact of the moulding wall with the heated mould surface is arranged at
75 temperatures and for times adapted to obtain a desired partial crystallinity of the plastics material.
7. Method according to claim 6, characterised in that the plastics material of the semifinished object is maintained substantially in its amorphous state during stabilization and during the first thermal conditioning process.
8. Method according to claim 6, characterised in that the plastics material of the semifinished object during stabilization and during the first thermal
85 conditioning process is already subjected to a first, slight crystal growth.
9. Method according to any of the claims 6 to 8, characterised in that the mould surface is maintained at a temperature in a region below to above the temperature for optimum crystal growth in the appropriate plastics.
10. Method according to claim 9, characterised in that the mould surface is maintained at a temperature in the region of the temperature required for
95 optimum crystal growth in the appropriate plastics.
11. Method according to any of the claims 1 to 10, characterised in that during the first thermal conditioning process and/or between the first thermal conditioning process and thermal forming, and while substantially retaining the crystallinity state of
100 its plastics, the semifinished object is subjected to stretching, more particularly biaxial stretching, as an additional physical effect.
12. Method according to any of the claims 6 to 11, characterised in that in the course of producing mouldings from polyethylene-terephthalate
A temperature in the region of 50° to 100°C is adjusted for stabilization and the first thermal conditioning process of the semifinished object and
110 A temperature in the region of 120° to 180°C is maintained on the mould surface.
13. Method according to claim 1, characterised in that
During stabilization and the first thermal conditioning process the surface regions of the semifinished object are adjusted to hardening temperatures suitable for handling the semifinished object and the interior thereof is adjusted to temperatures suitable for optimum crystal growth in the appropriate plastics material and
120 Thermal forming takes place on at least one mould surface which is heated to a temperature at which crystal growth occurs in the appropriate plastics.
14. Method according to claim 13, characterised in that the plastics material in the interior of the semifinished object is arranged by the effect of the adjusted temperature and duration of the first thermal conditioning process to form a crystallinity state at which the appropriate plastics is still thermally
130 deformable.

15. Method according to claim 13, characterised in that the plastics in the interior of the semifinished object is converted by the effect of the adjusted temperature and the duration of the first thermal conditioning process into a crystallinity state which is beyond the limit of the actual thermal deformability of the appropriate plastics.

16. Method according to any of the claims 13 to 15, characterised in that the mould surface is heated to a temperature suitable for optimum crystal growth in the appropriate plastics material.

17. Method according to any of the claims 13 to 16, characterised in that in the course of producing mouldings from polyethylene terephthalate

15 The surface region temperature is adjusted to approximately 50° to 100°C and the temperature of the internal region is adjusted to approximately 140° to 160°C during stabilization and the first thermal conditioning process of the material web and

20 The mould surface is heated to approximately 120° to 180°C for the thermal forming and second thermal conditioning process.

18. Method according to claim 1, characterised in that

25 During stabilization and the first thermal conditioning process the cross-sectional surface regions of the semifinished object are adjusted to temperatures for hardening suitable for handling of the semifinished object and the interior is left substantially at the plasticizing temperature used for extruding the material web;

Thermal forming takes place on at least one mould surface which is heated to a temperature at which crystal growth occurs in the appropriate plastics material and

35 For the purpose of the second thermal conditioning process the moulding wall is maintained for a time, adapted to the desired final crystallinity state of the moulding wall, at a temperature at which crystal growth takes place in the plastics material of the moulding wall.

19. Method according to claim 18, characterised in that the temperature on the mould surface is adjusted slightly below the temperature for optimum crystal growth and during the second thermal conditioning process the moulding is maintained at a temperature which is in the temperature range for optimum crystal growth.

20. Method according to claim 18 or 19, characterised in that the plastics material in the surface regions of the semifinished object is substantially maintained in the amorphous condition during stabilization and during the first thermal conditioning process.

21. Method according to claim 18 or 19, characterised in that during stabilization and the first thermal conditioning process the plastics material in the surface regions of the semifinished object is converted into a predefined and slightly partially crystalline state.

22. Method according to any of the claims 18 to 21, characterised in that during the production of mouldings from polyethylene terephthalate

The surface region temperature of the material web during stabilization and during the first thermal

conditioning process is adjusted to approximately 80° to 100°C and the temperature in the interior of the web is allowed to remain at approximately 250° to 300°C and

70 During thermal forming and during the second thermal conditioning process the mould surface is kept at a temperature of approximately 140° to 160°C.

23. Method according to any of the claims 6 to 22, characterised in that the moulding wall is maintained in contact with the mould surface for the second thermal conditioning process.

24. Method according to any of the claims 6 to 22, characterised in that during the second thermal conditioning process the moulding is removed from the mould surface and is subjected to an ensuing heat treatment.

25. Method according to claim 23 or 24, characterised in that the plastics material of the moulding wall is substantially converted into its crystalline state during the second thermal conditioning process.

26. Method according to claim 23 to 25, characterised in that during the second thermal conditioning process the moulding wall is maintained at a substantially uniform temperature.

27. Method according to any of the claims 23 to 25, characterised in that during the second thermal conditioning process the moulding wall is heat treated at a temperature which diminishes with respect to time.

28. Method according to claim 27, characterised in that temperature control during the second thermal conditioning process is applied substantially in the form of cooling based on temperatures for optimum crystal growth in the appropriate plastics material.

29. Method according to any of the claims 1 to 28, characterised in that thermal forming is performed by the application of mould pressure on the plastics material of the moulding wall.

30. Method according to any of the claims 1 to 29, characterised in that between extrusion and thermal forming the semifinished object is subjected to calendering or rolling accompanied by thickness reduction to provide an additional physical effect to influence the crystallinity state.

31. Method according to claim 30, characterised in that the calendering or rolling operation is included in the operation of stabilizing the semifinished object.

32. Method according to any of the claims 1 to 31, characterised in that glycol modified polyethylene terephthalate is used as thermoplastic production material.

33. Method according to any of the claims 1 to 31, characterised in that polybutylene terephthalate is used as thermoplastics production material.

34. Apparatus for performing the method according to any of the claims 1 to 33 with an extrusion device for the continuous production of the semifinished object, a stabilizing device for the semifinished object and thermal forming means and, where appropriate, a device for cutting the mouldings from the surrounding portions of the

semifinished object, characterised by the following features:

A first thermal conditioning station (14) is disposed between the stabilizing device (13) and the thermal forming device (16);

The thermal forming device (16) is disposed in a second thermal conditioning station (17);

The stabilizing device (13) and the thermal forming device (16) are provided with control means for the predefined and where appropriate programmable regulation of the physical and more particularly thermal effects which act on the plastics material of the semifinished object (10) and take place in the stabilizing device (13) and in the thermal forming device (16) and

The thermal conditioning stations (14, 17) are associated with means for producing physical, more particularly thermal effects on the plastics material of the semifinished object (10) or moulding (18) and said conditioning stations are also associated with control means for the predefined and where appropriate programmable regulation of the effect producing means.

35. Apparatus according to claim 34, characterised in that the thermal conditioning stations (14, 17) contain heating and cooling means for the semifinished object (10) or the mouldings (18) with regulating facilities for temperature and heating or cooling time.

36. Apparatus according to claim 34 or 35, characterised in that the first thermal conditioning station (14) is associated with a stretching device for the semifinished object (10) and with means for regulating the stretching temperature, the degree of stretching and where appropriate the stretching rate.

37. Apparatus according to claim 36, characterised in that the stretching device is constructed for biaxial stretching of a web-shaped or tubular semifinished object (10).

38. Apparatus according to any of the claims 34 to 37, characterised in that the stabilization device (13) is associated with means for calendering and/or rolling of a web-shaped semifinished object to reduce the thickness thereof.

39. Apparatus according to any of the claims 34 to 38, characterised in that the cooling means provided in the stabilization device (13) are equipped with means for producing variable temperature control in time sequence adapted to act on the plastics material of the semifinished object (10).

40. Apparatus according to any of the claims 34 to 39, characterised in that the thermal forming device (16) contains at least one mould with a variable heatable and coolable mould surface.

41. Apparatus according to any of the claims 34 to 40, characterised in that the thermal forming device (16) contains at least one mould which is equipped with control means for producing a predefined and where appropriate programmable temperature change or temperature control with respect to time on at least one mould surface during the thermal forming process.

42. Method according to any of the claims 34 to 41, characterised in that the thermal forming device (16) contains at least one mould which is equipped

with means for producing a predefined controllable mould pressure.

43. Apparatus according to claim 42, characterised in that the means for generating the mould pressure are equipped with a control device for the controllable and where appropriate programmable changing of the mould pressure with respect to time during the thermal forming process.

44. Apparatus according to any of the claims 34 to 42, characterised in that the inlet region of the second thermal conditioning station (17) contains the thermal forming device (16) and extends beyond the exit of the thermal forming device (16).

45. Apparatus according to claim 44, characterised in that the second thermal conditioning station (17) contains a heat treatment device for the mouldings adjoining the outlet of the thermal forming device (16).

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